tively. The corresponding values for SO_2 in $CHCl_3$ are -4.9 and -2.02 kcal/mole. Values of -16.4 and -8.33 kcal/mole are calculated for the energy and free energy of transfer of the complex from vapour to chloroform.

The results we have reported for the TMA—SO_2 systems afford the first example of a *CT* complex for which the increase in K_c in polar solvents is accompanied by an increase in $-\Delta H°$ which definitely lies outside the experimental uncertainty in the enthalpy values. We believe, however, that when more accurate values of $\Delta H°$ become available for a number of strong *CT* complexes, it will be generally observed that $-\Delta H°$ and K_c vary in the same direction as the solvent is changed. The resonable explanation for the increased value of the equilibrium constant in polar solvents, in terms of enhanced interaction between the dipole of the complex and the environment, implies that the magnitude of $\Delta H°$ for complex formation should also increase. In hydrogen-bonded systems, it has almost invariably been noted that $\Delta H°$ and $\Delta G°$ vary in the same direction as the medium is varied.[9]

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Ion Pair Extraction in Preparative Organic Chemistry

VI. Alkylation of Acetylacetone

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The alkylation of acetylacetone presents an interesting preparative problem. The anion of acetylacetone is a rather weak nucleophile and acetylacetone is alkylated much slower than ethyl acetoacetate and diethyl malonate. In a protic solvent the reaction is usually too slow to give an acceptable reaction time. In an aprotic solvent such as DMSO the rate is acceptable, but the main product is now the *O*-alkylated product.[1] In some recent publications it has been demonstrated that *O*-alkylation also occurs to some extent under other conditions.[2] The best compromise to date is to use acetone as a solvent and K_2CO_3 as the base, although the reaction time is still very long (20 hours for methylation).[3] The time can be considerably decreased using Rb_2CO_3 or Cs_2CO_3 as the base,[4] but these are too expensive for routine use. The tetrabutylammonium ion behaves like a large alkali ion in many reactions. It can be expected therefore, that the tetrabutylammonium salt of acetylacetone is very rapidly alkylated.

We have recently demonstrated that tetrabutylammonium salts are readily prepared by ion pair extraction,[5] and that the salt of methyl cyanoacetate is rapidly alkylated in a chloroform solution.[6] We have now applied the same method to acetylacetone. Even in the present case the reaction is very rapid and the alkylations are quantitative in every case presented in Table 1. The percentage of the *O*-alkylated product is similar to that reported in the reference mentioned above.[2]

The identity of the alkylated products, with the exception of 3-butylacetylacetone, was ascertained by comparison with authentic samples by means of NMR and VPC. 3-Methyl- and 3-ethylacetylacetone were prepared by acetylation of the corresponding ketone with acetic an-

Table 1.

Alkylation agent	R $CH_3COCHCOCH_3$	R $CH_3COCCOCH_3$ R	OR $CH_3C=CHCOCH_3$	Reaction time min
Methyl iodide	98.5[a]		1.5	10
Ethyl iodide	72	16	12	15
Isopropyl iodide	50.5		49.5	30
Butyl iodide	87		13	15

[a] The conventional procedure in methylation of acetylacetone is reported to yield a product containing about 10 % of 3,3-dimethylpentane-2,4-dione.[3,4] We did not succeed in separating the methylated products by gas chromatography. The enolization of the products made the NMR-spectrum very complicated. The figure in Table 1 therefore is the sum of mono- and dimethylated products.

hydride in the presence of boron trifluoride.[7] This gives a product free from *O*-alkylated compounds but which contains small quantities of the isomers 2,4-hexanedione or 2,4-heptane-dione. 3-Isopropylacetylacetone was synthesized according to the method described in *Org. Syn.*[8] A product rich in 4-methoxypent-3-en-2-one can be prepared in acceptable yields by alkylation of acetylacetone with dimethyl sulphate in DMSO, analogously with the method described by Joffe.[2] Dialkylated products were prepared by alkylation of the substances obtained from the work referred to above [7,8] by the same method as that used for acetylacetone. The gas chromatographic analyses were carried out directly on the evaporated reaction mixture by means of a 2 m × 1/8″ column packed with carbowax 20 M (5 %) at 160°C, with 40 ml/min N_2 flow.

Experimental. Tetrabutylammonium salt of acetylacetone. 0.5 Mole (170 g) of tetrabutylammonium hydrogen sulphate was added to a cooled solution of 1.1 mole of sodium hydroxide in 500 ml of water. 0.5 Mole (50 g) of acetylacetone was added and the solution was extracted with 500 ml of chloroform. The chloroform layer was evaporated and the crystalline residue was recrystallized from acetone. The yield of the salt was 70 % and the melting point 155°C.

Alkylation procedure. The double excess of alkyl iodide was added to a stirred solution of the tetrabutylammonium salt of acetylacetone in chloroform as reported in the alkylation of methyl cyanoacetate.[6] The chloroform and the excess of alkyl iodide were evaporated and the tetrabutylammonium iodide precipitated by adding ether to the residue. After filtration the ether was evaporated and the residue analysed as described above.

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